Report for 2002KY4B: Occurrence and distribution of mercury in Mammoth Cave National Park

- Conference Proceedings:
  - Webb, Cathleen J., Gretchen E. Berryman, Melissa A. Petty, Glenda H. Jones, and Stephen V. Hartman, 2003, Occurrence and Distribution of Mercury in Mammoth Cave National Park - Phase 0, in Proceedings Kentucky Water Resources Annual Symposium, Kentucky Water Resources Research Institute, University of Kentucky, Lexington, Kentucky, p. 59-60.

Report Follows:

Problem and Research Objectives

Atmospheric deposition of mercury from power plant emissions, a major input of mercury into the environment, is coming under closer scrutiny by regulatory agencies. With increasing demand for power, applications for many new coal-fired power plants are currently being considered. Consequently, an understanding of the existing levels of mercury is critical, particularly in a karst aquifer system (such as in South-central Kentucky) where transport of contaminants can be rapid. Mammoth Cave National Park (MCNP) is affected by the atmospheric deposition of mercury, contributed to by coal burning power plants. With over twenty new power plant applications under consideration in the Commonwealth of Kentucky, significant increases in mercury deposition to the park and surrounding area can be expected.

The overall vision and scope of this project were to understand the physical and geochemical processes that govern the fate and transport of mercury in a karstic aquifer system. Mercury mobility in surface water and ground water are of great concern because of toxic effects on the environment. Mercury is a persistent, bioaccumulative toxin, with significant impacts on aquatic species, such as mussels. The specific research project examines mercury transport in ground water and surface water in Mammoth Cave National Park. Water sampling results will be complemented by an investigation of the extent of bioaccumulation of mercury in fish and mussels and the levels and distribution of mercury in fish and mussels will be correlated with concentrations of mercury measured in the atmosphere, water, and sediments of the study site.

The specific objectives of this work were to: (1) establish the extent, occurrence, and distribution of mercury in groundwater, surface water and sediments in Mammoth Cave National Park, (2) determine the levels of mercury (a persistent bioaccumulative toxin) in fish and mussels in the Park in order to compare the mercury levels in fish and mussels to the health, diversity, population, and reproductive status of the species, and (3) investigate the fate and transport characteristics of mercury in a karst aquifer system. Objectives 1 and 2 have been actively pursued over the course of this project. Experimental work for objective 3 will be completed during summer 2003.

Methodology

Water samples were collected monthly and analyzed for mercury. Sediment samples were collected and analyzed on a seasonal basis. Rainfall was measured on a daily basis. Mercury analysis was done using Leeman Hydra atomic absorption (Hydra AA) spectrometry. The samples are digested using the Leeman Hydra Prep to convert all forms of mercury into Hg^{2+} and to eliminate the existence of any organic substance.

Procedure for sample digestion:

1) Sample mass determined and placed into a sample cup.
2) 2.25 mL concentrated AquaRegia (3:1 HCl: HNO_3) was added.
3) The sample cup was heated at 95 ^{o}C for 2 minutes in a water bath.

4) After the sample cooled, 6.75 mL 5% $KMnO_4$ was added.
5) 4.5 mL deionized (DI) water was added.
6) A second aliquot of DI water (4.5 mL) water was added.
7) The sample was heated in the water bath at 95 ^oC for 30 minutes.
8) After the sample cooled, 3.6 mL 12%:12% NaCl:hydroxylamine sulfate was added.

Procedure for sample analysis:

The concentration of mercury (ppt for water samples and ng/g for sediment samples) was determined by Leeman Hydra Atomic Absorption:

1) The spectrometer was calibrated with standard solutions.
2) The sample was withdrawn by a pump and mixed with the 10% $SnCl_2$:10% HCl solution, which ensures Hg^{2+} was reduced to Hg^0 , a volatile species.
3) In a liquid/gas separator, the mixed solution was bubbled by ultra high purity nitrogen and the mercury vapor was carried to pass through a dryer to dehumidify the gaseous mixture. The dry mercury vapor then entered a dual beam optical cell, which had been optimized for fast response time and high sensitivity. A mercury lamp controlled by the error signal of the reference beam delivered a stable source of emission at 254nm. Absorbance by the mercury cold vapor was measured using a solid state detector with a wide dynamic range.

The analytical results were organized into tables and graphs based on sample site location, mercury concentration, and the sampling month.

Samples of drum, a long-lived bottom feeding species, large mouth bass, and Corbicula *fluminea* the Asiatic clam were homogenized and analyzed for mercury using the same methods as sediment. Muscle tissue and liver from both types of fish were analyzed. The mercury concentrations of these water species were compared to other freshwater species according to the U.S. Food and Drug Administration Center for Food Safety and Applied nutrition Office of Seafood, 2001.

Principal Findings and Significance

Results of sampling and analysis of the water, sediment, and aquatic life of the park indicate detectable levels of mercury. As expected, mercury levels in water are generally low (0 - ~20 ppt) since mercury preferentially binds to sediments and organic material. Ugly Creek Spring and Bush Island sampling locations show peak levels of mercury in the 30 – 40 ppt range. Seasonal changes and precipitation levels affected the concentration of mercury that was detected in the water. Samples collected on days with high precipitation showed higher levels of mercury. Mercury concentrations observed in sediments ranged between 0 – 100 ppb. Pike Spring, Mile 205.7 Spring, and Big Spring all show consistent high levels of mercury in sediments (30 – 70 ppb range). These sites are all located in the upstream portion (Green River) of the sampling area. The 0.233 ppm mercury found in the muscle of the Drum fish illustrates the potential threat of mercury to the food chain. These fish are long-lived bottom feeders, and are vulnerable

to bioaccumulation of mercury from aquatic organisms, ground water, and sediment layers in MCNP. The observed mercury levels in Drum are comparable to those seen in other species that are considered within the safety limits of the U.S. Food and Drug Administration, but may indicate the potential for future increases that could pose a threat to the ecosystem.